

Chemical vapor deposition of Co_3O_4 on honeycomb substrates for catalytic applications

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Inexpensive cobalt oxide, Co_3O_4 , is known as the most active binary oxide catalyst for the oxidation of hydrocarbons (1-3). Chemical Vapor Deposition, CVD, is a promising method to coat 3D substrates. In this work, the deposition of Co_3O_4 on cordierite honeycomb substrates and their catalytic activity was studied.

Honeycomb cordierite substrates were deposited with Co_3O_4 in a hot-wall CVD reactor in the temperature range between 200°C to 400°C. $\text{Co}(\text{acac})_2$ and oxygen were used as precursors. Useful coatings were obtained at reduced pressure (50 mbar) and increased flow rates (0.05 slm N_2 as carrier gas and 4 slm O_2) resulting in a gas velocity of 2.5 m/s. Nevertheless, a gradient in film thickness along the axial direction was visible (Fig. 1). To reduce this gradient, samples were turned around to be coated from both sides. The morphology of the samples was studied by SEM. Some of the samples were examined with XRD.

At temperatures between 200°C and 250°C, the deposition got thicker due to the surface-controlled growth mechanism (4). For samples in the mass-transfer-controlled temperature range ($T_{\text{Dep}} > 250^\circ\text{C}$), the gradient increased with rising deposition temperatures. These samples showed thick deposits in the first 1 cm to 2 cm of the substrate. Only in this entrance area crystalline structures larger than 100 nm grew. This morphology was not stable at the high temperatures used in the catalytic tests. The sharp crystals changed to an amorphous surface.

The catalytic activity of the coated samples was tested in a fixed bed reactor in the temperature range between 275°C and 750°C at a pressure of 980 mbar. Methane and synthetic air were mixed to a fixed mole fraction, $x_{\text{methane}} = 3.7\%$. The total gas flow was varied between 57 sccm and 1090 sccm, resulting in space velocities between 1590 1/h and $1.15 \cdot 10^5$ 1/h. All samples were catalytic active with best samples deposited at low temperatures of 200°C and 250°C (Fig. 2), caused by a minor deposition gradient. These samples showed promising performance at low gas flows (Fig. 3); they were more active than wet-coated samples obtained by a conventional procedure.

The catalyst's long-term stability was also investigated keeping the catalyst at a constant temperature, $T_{\text{cat}} = 600^\circ\text{C}$ or $T_{\text{cat}} = 680^\circ\text{C}$. The activity of all catalysts was considerably reduced with half-life periods of less than 300 min. This can be explained by morphology changes (above mentioned) to amorphous surfaces with fewer catalytically active centers at high temperatures.

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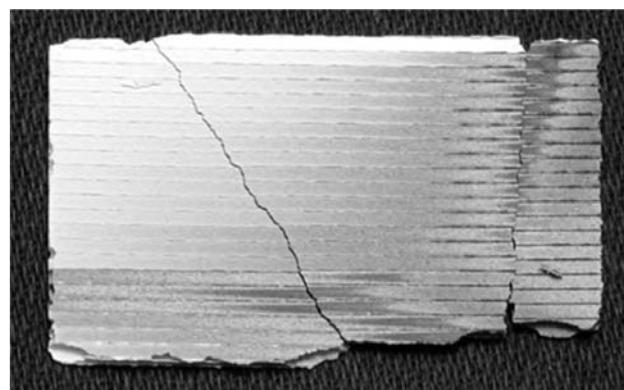


Figure 1: longitudinal sample section deposited at $T_{\text{Dep}} = 250^\circ\text{C}$, deposition time: 6h.

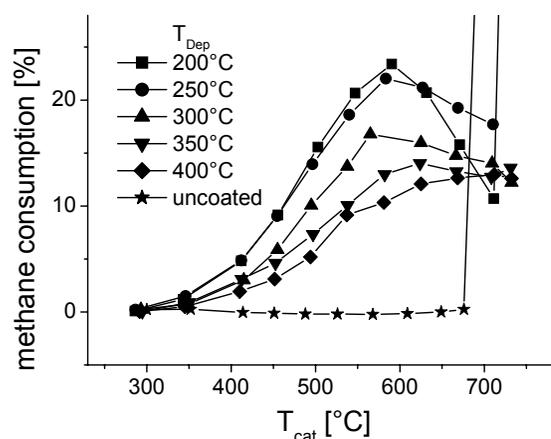


Figure 2: Catalytic methane consumption of double-sided deposited substrates with 3 h deposition time for each side

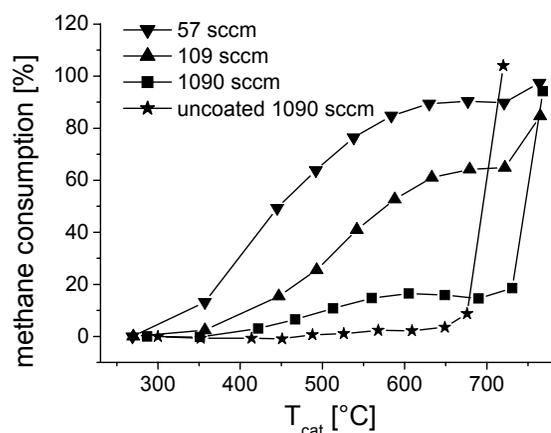


Figure 3: Flow dependency of the catalytic methane consumption of double-sided samples, $T_{\text{Dep}} = 250^\circ\text{C}$, total deposition time: 6 h.